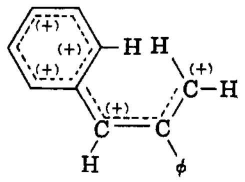

XI

rate at which it is consumed by reduction, is converted in part to the *cis* ion (40–70% conversion in reductions at room temperature). We may, in general, then, expect that one geometrical isomer of an allylic alcohol will be reduced with a high degree of retention of geometric configuration, but that the other isomer will give sizeable amounts of the same products, the nature of these products being determined, first, by the relative stability of the two allylic carbonium ions (*not* to stability of the olefins) and, second, by the extent to which reduction occurs at either end of the allylic systems. The use of this reaction in the assignment of configuration is, thus, not without hazard, and some care should be exercised in its use for this purpose.

Hydrogenolyses with Chloroaluminum Hydrides. II. Benzylic Alcohols

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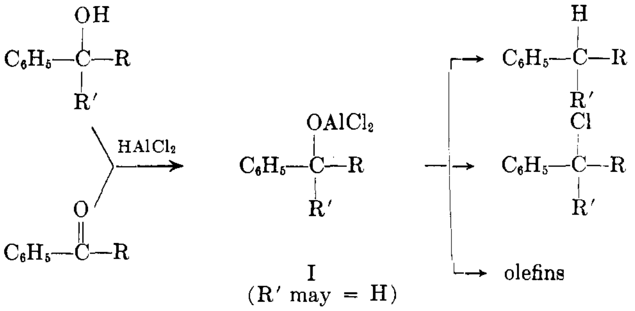
Benzylic alcohols are reduced to hydrocarbons by mixtures of aluminum chloride and lithium aluminum hydride. The ease of reduction is sensitive to the structure of the alcohol and the Lewis acidity of the reagent, the influence of these factors suggesting that the slow step involves formation of a benzylic carbonium ion. Chlorides, which may be formed in a side reaction, appear to be reduced more slowly than alcohols by "dichloroaluminum hydride." Olefins are prominent by-products in the reduction of tertiary benzylic alcohols; in at least one case the elimination reaction follows the Hofmann rule.

Since allylic alcohols undergo hydrogenolysis with mixtures of aluminum chloride and lithium aluminum hydride,[2] it seemed likely that benzylic alcohols would also undergo this reaction. Hydrogenolysis of activated aromatic carbinols has been observed to occur with excess lithium aluminum hydride alone at temperatures of 60–90°.[3] Reductions in which such hydrogenolysis might reasonably be considered to be the final step have been reported to occur when aromatic acids, aldehydes, and ketones are treated with "mixed hydride" reagents.[4,5] The latter papers, however, give the impression that carbinols are not always intermediates and may well be reduced less easily than carbonyl compounds. Thus Nystrom and Berger[5] report that methylphenylcarbinol is not reduced when treated with a large amount of a reagent that reduces acetophenone to ethylbenzene; they also report that benzyl alcohol is not reduced although triphenylcarbinol and benzhydrol are reduced with ease. Brown and White[4] suggest that reduction to the carbinol stage may be a deleterious side reaction leading to the formation of chlorides and olefins. We have, therefore, investigated this matter in more detail and have found that benzylic alcohols in general can be reduced by "mixed hydrides" (Table I). This indicates that the alcohols or, more probably, alkoxyaluminum compounds derived from them (as I) are at least sufficient as intermediates in the reduction of the more highly oxidized compounds. In several cases it was observed that alcohols and ketones are essentially equivalent as starting materials in preparative applications of this reaction.



In accord with an earlier report[5], we found that benzyl alcohol was not detectably reduced by 3:1 reagent[6] after three days in refluxing diethyl ether; it was reduced (in part) to toluene at 70–80°. Under these conditions a higher-boiling product, apparently identical with that formed on benzylation of toluene, also was obtained. In contrast, *p*-methoxybenzyl alcohol was cleanly reduced to *p*-methoxytoluene in half an hour at room temperature, confirming the strong activating effect of methoxy groups observed by Conover and Tarbell[3] and by Brown and White.[4] Methylphenylcarbinol also was more easily reduced than benzyl alcohol. With excess 3:1 reagent the alcohol was almost completely consumed in two hours at room temperature, but virtually no reduction occurred when the ratio of chloride to hydride was low (Table II). We have calculated the chloride-to-hydride ratios obtaining in the reaction mixtures used by Nystrom and Berger[5], assuming rapid formation of I, and find (Table III) that their experimental results are consistent with ours. When the chloride-to-hydride ratio was higher than 2, acetophenone was reduced to ethylbenzene; when it was lower, the ketone was reduced only to the alcohol in the short reaction time allowed. Their failure to obtain hydrogenolysis with the alcohol is now seen to have resulted from the use of *too much* of their 1:1

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[1] The authors gratefully acknowledge the financial support of this research by the National Science Foundation (Grant NSF-G 10051).

[2] J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 116 (1964). References to earlier examples of this reaction are cited in this paper.

[3] L. H. Conover and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 3586 (1950).

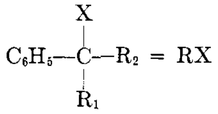
[4] B. R. Brown and A. M. S. White, *J. Chem. Soc.*, 3755 (1957).

[5] R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

[6] This is the molar ratio of aluminum chloride to lithium aluminum hydride used in preparing stock solutions[2] of "mixed hydride" reagents. The 3:1 reagent has the composition of $AlCl_2H$ and also will be referred to as "dichloroaluminum hydride." In most of this work we have used amounts of this reagent corresponding to 4 moles of this species per mole of alcohol.

TABLE I

HYDROGENOLYSIS OF BENZYLIC ALCOHOLS AND CHLORIDES (3:1 REAGENT)[a]



$C_6H_5—\overset{\displaystyle X}{\overset{|}{\underset{\underset{\displaystyle R_1}{|}}{C}}}—R_2 = RX$

R_1	R_2	Temp., °C.	Time, hr.	% RX reacted	Reaction product, % composition[b] RH	RCl	Olefin
			X = OH				
H	H	*ca.* 40	72	0			
		ca. 75	24		48 (isolation)		
H[c]	H[c]	*ca.* 25	0.5	*ca.* 100	*ca.* 100		
H	CH_3	*ca.* 25	2	97	74	14	12
CH_3	CH_3	*ca.* 25	4	100	56		44
$-(CH_2)_5-$		*ca.* 25	4	100	56		44
H	$C(CH_3)_3$	*ca.* 25	0.5	2	13	87	
		ca. 25	4	4	38	62	
		ca. 40	24	57	56	44	
		ca. 40	92	100	83	17	Trace
H	*e*-$\underset{\underset{\displaystyle CH_3}{|}}{CH}—C_6H_5$[d]	*ca.* 25	3	89	61	39	
		ca. 25	24	100	96	4	
H	*t*-$\underset{\underset{\displaystyle CH_3}{|}}{CH}—C_6H_5$[d]	*ca.* 25	0.2	97	68	32	
		ca. 25	3	100	72	28	
		ca. 25	24	100	96	4	
CH_3	$CH_2C_6H_5$	*ca.* 25	0.05	93	13	+	+
		ca. 25	2	100	39	0	61[e]
		ca. 25	4	100	39	0	61[e]
		0	48	100	39	0	61[e]
			X = Cl				
H	*e*-$\underset{\underset{\displaystyle CH_3}{|}}{CH}C_6H_5$[d]	*ca.* 25	3	7	100		
H	*t*-$\underset{\underset{\displaystyle CH_3}{|}}{CH}C_6H_5$[d]	*ca.* 25	3	18	100		
CH_3	$CH_2C_6H_5$	*ca.* 25	3	100	52		48[f]

[a] See ref. 6. [b] Analysis by gas chromatography unless otherwise noted. [c] *p*-Methoxybenzyl alcohol. [d] *e*-, *erythro;* *t*-, *threo.* [e] 21% *trans*-α-methylstilbene; 79%-α-benzylstyrene. [f] 58% *trans*-α-methylstilbene; 42% α-benzylstyrene.

TABLE II

HYDROGENOLYSIS OF METHYLPHENYLCARBINOL

Reactants, mole/mole of alcohol $AlCl_3$[d]	$LiAlH_4$[e]	Ratio, Cl–H[a]	% reaction[b,c]	Product composition,[c] % EB[f]	S[f]	PEC[f]
1	1	1	2	66	15	19
1	1	1	52[g]	76[g]	14[g]	10[g]
2	1	2	75	71	14	15
3	1	3	97	74	12	14
4	1	4	100	74	14	12
4	1	4	100[h]	73[h]	14[h]	13[h]
5	1	5	100	74	14	12
2.67[i]	1.67[i]	1.41[i]	0[i]			

[a] Ratio after assumed formation of alkoxide I. [b] In ether at room temperature; 2 hr. except where noted. [c] Analyses by v.p.c. on Carbowax 20 M at 120° with preheater at 140°. At higher temperatures some of the chloride cracked to form styrene. [d] 1 *M* $AlCl_3$ in ether. [e] 0.25 *M* $LiAlH_4$ in ether. [f] EB, ethylbenzene; S, styrene; PEC, α-phenylethyl chloride. [g] 18 hr. [h] Acetophenone as starting material. [i] Data of Nystrom and Berger[5]; reaction presumably carried out in refluxing ether for 1 hr.

TABLE III

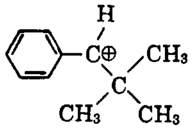
HYDROGENOLYSIS OF ACETOPHENONE[a]

Reactants, mole/mole of ketone $AlCl_3$	$LiAlH_4$	Ratio, Cl-H[b]	Product, %[c] Alcohol	Ethyl benzene
1	1	1.0	91	..
0.77	0.77	1.11	93	..
1.77	0.77	2.6		25
2.75	0.75	4.13		56
4[d]	1[d]	4[d]		74[d]

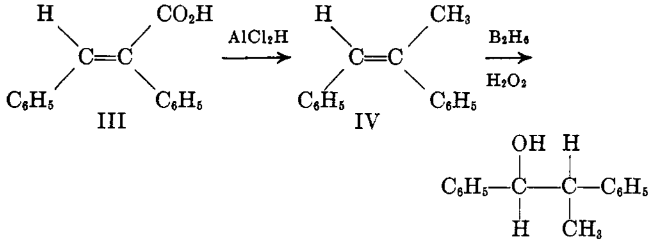
[a] Calculated from data of Nystrom and Berger.[5] [b] Ratio after assumed reduction and formation of alkoxyaluminum intermediate (I). [c] Isolation after about 1 hr. in refluxing ether. [d] This work; 5 hr. at room temperature; product obtained by isolation.

reagent,[6] which is too rich in hydride to be effective with this alcohol. Their finding that triphenylcarbinol and benzhydrol were reduced with ease by this reagent may then be taken as evidence that additional phenyl groups promote hydrogenolysis even more strongly than does a methyl group. The importance of Lewis acidity (as judged by the chloride–hydride ratio) and of substituents in promoting the reduction of benzylic alcohols indicate that a high degree of carbonium ion character is developed in the transition state for the slow step of this reaction, as does the formation of benzyltoluenes in the reduction of benzyl alcohol.

t-Butylphenylcarbinol was found to be considerably less reactive than methylphenylcarbinol though more reactive than benzyl alcohol (Table I). In this case the product was initially rich in unrearranged chloride, but the amount of chloride in the reaction product decreased as the reaction proceeded, indicating that the chloride was slowly reduced. The final hydrocarbon product was nearly pure (96%) neopentylbenzene. The virtual absence of rearrangement does not exclude the formation of a carbonium ion; a number of compounds of this series undergo solvolysis reactions (presumably *via* II) without rearrangement.[7,8] An increase in the steric interaction of the phenyl and *t*-butyl groups in the formation of II previously has been invoked to account (in part) for the relatively slow solvolysis of the tosylate and chloride[8]; a similar explanation seems appropriate for the relatively slow reduction of both the alcohol and the chloride observed here.

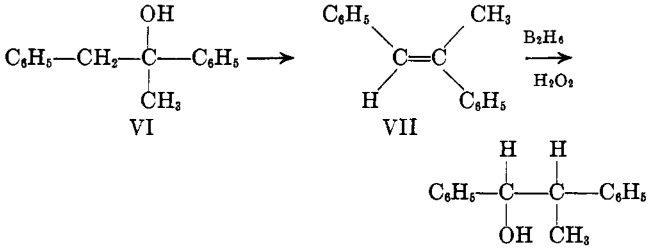


II



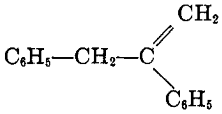
III IV

threo
V



VI VII

erythro
VIII



IX

Chlorides also play a role in the hydrogenolysis of the 1,2-diphenyl-1-propanols (*threo*, V; *erythro*, VIII).[9] Both alcohols gave nearly pure 1,2-diphenylpropane on treatment with excess 3:1 reagent[6] in ether at room temperature for one day. Virtually no olefins were detected in the product, indicating that none were formed at any point in the reaction, the possible olefins being neither reduced nor isomerized by 3:1 reagent.[2] When the reaction was interrupted after three hours, the presence of some 28–35% of olefins was indicated by gas chromatographic analysis. This we attribute to the presence of the chlorides since they (but not the alcohols) were found to give similar olefin mixtures on gas chromatography, apparently cracking quickly and cleanly in the preheater. The conclusion that appreciable amounts of chloride were formed is supported by our observation that the *erythro* chloride[10] can be prepared from the *erythro* alcohol by reaction with 3:1 reagent at ice temperature (seven days). Both of the chlorides were separately prepared and treated with 3:1 reagent; some reduction occurred in each case (Table I), but it is clear that this reduction is so slow that the chlorides cannot be major intermediates in the reduction of the alcohols. Thus, the *threo* alcohol (V) gave 66% of 1,2-diphenylpropane in thirteen minutes while the *threo* chloride gave only 18% in three hours. It is seen that the formation of chlorides is deleterious in the sense that it diverts a portion of the starting material into a pathway that leads to slow formation of hydrogenolysis product; the effects of this side reaction can be overcome by allowing time for reduction of the chlorides to occur. Attack of a hydride donor on a free carbonium ion would provide a more direct and, we suggest, a more rapid route to the reduction product.

Dimethylphenylcarbinol and 1-phenylcyclohexanol, two simple tertiary benzylic alcohols, were rapidly converted to hydrocarbons by 3:1 reagent at room temperature (Table I). In each case a pronounced evolution of hydrogen gas occurred during the first hour of the reaction, and in each case the product contained about 44% of olefin. 1,2-Diphenyl-2-propanol (VI) also reacted rapidly, the product obtained after thirty minutes of reaction being free of alcohol (v.p.c.) and chloride (negative Beilstein test) and identical with that obtained after two or four hours reaction time. This product contained 39% of 1,2-diphenylpropane, 13% of *trans*-α-methylstilbene (VII), and 48% of α-benzylstyrene (IX). The high proportion of IX in the olefinic product indicates that elimination with "dichloroaluminum hydride" is not controlled by the thermodynamic stability of the olefinic product,[11] but by the steric requirements of the leaving group.[12] Eliel[13] has suggested that the oxygen atom of a species such as I, with its inorganic burden, acts as a very bulky group in epimerizations of alcohols. The steric requirement of this group would be increased by attachment of an additional Lewis acid species preliminary to the formation of a carbonium ion.[2] It seems possible, then, that the elimination process involves loss of a proton from an ion pair; we do not, however, have data which exclude other possible explanations for the occurrence of Hofmann elimination.

We conclude that "mixed hydride" reagents are useful in the reduction of phenyl ketones and secondary benzylic alcohols, and that the alkoxides (I) are prob-

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(7) P. Skell and C. R. Hauser, *J. Am. Chem. Soc.*, **64**, 2633 (1942).

(8) S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

(9) Configurations have been assigned to these alcohols on the assumption that they give *cis* elimination in the formation of *cis*- and *trans*-α-methylstilbene (IV and VII) by the Chugaev reaction [D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952)]. The alcohols can be prepared conveniently from the α-methylstilbenes by hydroboration, the products being those to be expected from *cis* addition to the double bond [H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959); **83**, 2544 (1961)]. *cis*-α-Methylstilbene (IV) can be prepared in one step by reduction of the readily available *cis*-2,3-diphenylacrylic acid (III) with 3:1 reagent.[3]

(10) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5851 (1952), have prepared both chlorides and assigned configurations by use of stereospecific elimination reactions.

(11) These olefins are neither reduced nor isomerized by 3:1 reagent.[3] Equilibration of the α-methylstilbenes with acid or with strong base gives nearly pure *trans*-α-methylstilbene [D. J. Cram, F. D. Greene, and C. H. Depuy, *ibid.*, **78**, 790 (1956)] as does treatment of the tertiary chloride with aluminum chloride (see Experimental). Cracking of the chloride during v.p.c. gives 60% VII, 15% IV, and 25% IX, while reduction with excess 3:1 reagent gives 52% 1,2-diphenylpropane, 28% VII, and 20% IX. Hydrolysis with aqueous acetone or reaction with silver nitrate gives 70–80% of tertiary alcohol (VI) and an olefin mixture containing 53% VII, 5% IV, and 42% IX.

(12) See J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 186–206, for a discussion with many references.

(13) E. L. Eliel, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **22**, 129 (1961); E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

able intermediates in both cases. Time should be provided for the reduction of chlorides, which are formed in a separate reaction and which appear to be rather slowly reduced by these reagents. The formation of olefins is an important side reaction in the reduction of tertiary benzylic alcohols; this can be minimized by reduction of the chloride with a reagent rich in hydride (see Experimental).

Experimental

Unless otherwise specified reductions were carried out with stock solutions of 3:1 reagent[6] prepared by mixing ether solutions of lithium aluminum hydride and aluminum chloride at 0°, freed of sediment by decantation and stored at −4°. Most of the solutions used were about 1 *N* in hydride as found by measurement of the hydrogen evolved when an aliquot was treated with methanol. At the end of the reactions described subsequently the reaction mixtures (at room temperature or below) were poured onto at least an equal volume of ice. The ether layer was separated and the water layer was extracted with ether; the combined ether extract was washed with aqueous sodium carbonate and with saturated aqueous sodium chloride and then dried over anhydrous sodium sulfate. The solutions were concentrated by distillation of the ether through a Vigreux column or, in the 1,2-diphenylpropane series, by evaporation under vacuum, and then distilled at appropriate pressures and temperatures. Samples of all major products were purified by vapor phase chromatography (Aerograph Model A-90-C) and identified by comparisons of retention time, refractive index,[14] and infrared spectra with published data[15] or available authentic samples. Reaction mixtures and distillation fractions were analyzed by gas chromatography assuming 100% material balance. This assumption should be valid for materials obtained by distillation but would give high results if high molecular weight products were present in undistilled materials. In most cases the analytical results were reasonably consistent with yield data for products isolated by distillation. Chlorides of the 1,2-diphenylpropane series cracked in the v.p.c. preheater and gave clean analyses as mixtures of olefins. Microanalyses were performed by Dr. C. S. Yeh, Mrs. I. Groten, and Mrs. V. Keblys.

Hydrogenolysis of Benzyl Alcohol.—A solution of 5.4 g. (50 mmoles) of benzyl alcohol in 200 ml. (200 mmoles) of "dichloroaluminum hydride" reagent was heated at reflux for 3 days. An insoluble white solid formed, but no toluene could be detected by v.p.c. analysis of aliquots. About 150 ml. of diethyl ether was distilled and saved, the flask temperature rising to about 75°; the mixture was held at this temperature for 24 hr. It was then cooled to room temperature, and the ether distillate was added to the reaction mixture, which was then worked up in the usual way to give 2.2 g. (48%) of toluene, b.p. 109°, n^{20}_{D} 1.4962 (lit.[14a] n^{20}_{D} 1.4962), and 1.1 g. of a higher boiling fraction collected at 85–95° (1 mm.). A sample of this fraction was separated by v.p.c. on Carbowax 20 M at 200° to give about 10% of benzyl alcohol and a hydrocarbon fraction, n^{20}_{D} 1.5721, which, from microanalytical data (following) and comparisons of infrared spectra,[16] appears to be a 40:60 mixture (roughly) of 2-methyldiphenylmethane (lit.[16] n^{20}_{D} 1.5763) and 4-methyldiphenylmethane (lit.[16] n^{20}_{D} 1.5692).

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 8.03.

Alkylation of Toluene with Benzyl Alcohol.—A solution of 50 ml. (50 mmoles) of dichloroaluminum hydride reagent was diluted with 23 g. (250 mmoles) of anhydrous toluene, and then 2.70 g. (25 mmoles) of benzyl alcohol was added dropwise over a 2-min. period. The clear solution was heated to 80°, most of the ether distilling below 70°, and kept at about 80° for 10 hr. A white crusty solid separated and hydrogen evolution ceased after about 2 hr. The mixture was cooled in ice and shaken with 5 ml. of ice water until the solid had dissolved. An ether extract of the aqueous phase was combined with the toluene layer. The organic portion was dried, concentrated, and distilled to give 3.64 g. (80%) of mixed 2- and 4-methyldiphenylmethanes, b.p. 85–87° (1 mm.), n^{20}_{D} 1.5721, infrared spectrum superimposable on the mixture obtained from hydrogenolysis of benzyl alcohol (preceding).

Alkylation of Toluene with Benzyl Chloride.—Addition of 21 g. (230 mmoles) of anhydrous toluene to 24 ml. (24 mmoles) of dichloroaluminum hydride reagent caused precipitation of a granular white precipitate. Benzyl chloride (2.9 g., 23 mmoles) was added, and the solution was heated to 80° and held there for 10 hr. Worked up as before, this reaction mixture gave 2.7 g. (64%) of product, b.p. 85–87° (1 mm.), n^{20}_{D} 1.5721, infrared spectrum superimposable on those obtained previously.

Hydrogenolysis of *p*-Methoxybenzyl Alcohol.—In a small-scale run, 0.5 mmole of *p*-methoxybenzyl alcohol was treated with 2 ml. (2 mmoles) of dichloroaluminum hydride reagent for 0.5 hr. at room temperature. At this time conversion to *p*-methoxytoluene appeared to be complete as judged by v.p.c. analysis. A sample of product obtained by v.p.c. fractionation had n^{20}_{D} 1.5118 (lit.[17] $n^{19.3}_{\mathrm{D}}$ 1.5124).

Hydrogenolysis of Methylphenylcarbinol. A.—Reagents of varying aluminum chloride content were prepared by mixing appropriate amounts of 1.0 *M* aluminum chloride and 0.25 *M* lithium aluminum hydride in ether. One mole of carbinol was added for every mole of lithium aluminum hydride, and the solutions were let stand 2 hr. at room temperature, hydrolyzed, and analyzed by v.p.c. on Carbowax 20 M at 120° for hydrocarbons and chloride, at 150° for carbinol, assuming 100% material balance. The results are shown in Table II.

B.—On a preparative scale, 3.7 g. (30 mmoles) of methylphenylcarbinol and 120 ml. (120 mmoles) of dichloroaluminum hydride in ether were allowed to stand at room temperature for 5 hr. The mixture was hydrolyzed and distilled to give 2.7 g. (84%) of a hydrocarbon mixture which v.p.c. analysis showed to contain 12% of styrene and 88% of ethylbenzene. These components were isolated by v.p.c.: styrene, n^{20}_{D} 1.5457 (lit.[14b] n^{20}_{D} 1.5465), and ethylbenzene, n^{20}_{D} 1.4960 (lit.[14c] n^{20}_{D} 1.4960). The infrared spectra were identical with published ones (API No. 170 and 309).[15]

Essentially identical results were obtained when this experiment was repeated using acetophenone as the starting material.

C.—Methylphenylcarbinol (2.0 g., 0.016 mole) was added to a solution of 3:1 reagent made by mixing 20 ml. of an ether solution containing 6.0 g. (0.046 mole) of aluminum chloride and 12 ml. of 1.35 *M* lithium aluminum hydride (0.016 mole) in ether. The mixture was heated under reflux for 7 hr. and then poured on ice. The product was taken up in ether, and the ether extract was dried and analyzed by gas chromatography on a silicone column. Ethylbenzene was the only product evident, and comparison of retention times indicated the absence of styrene, α-phenylethyl chloride, and the starting alcohol. Under the same conditions acetophenone gave only ethylbenzene, but styrene was not reduced.

Hydrogenolysis of Dimethylphenylcarbinol.—Within minutes of mixing 0.34 g. (2.5 mmoles) of dimethylphenylcarbinol[18] (at least 99% pure by v.p.c.) and 10 ml. (10 mmoles) of 1 *N* ethereal dichloroaluminum hydride an insoluble layer separated. Vigorous evolution of hydrogen continued for about 0.75 hr. after the initial reaction of alcohol and reagent. The mixture was hydrolyzed after 4 hr. and analyzed and fractionated by v.p.c. on Carbowax 20 M, showing the formation of cumene (56%), n^{20}_{D} 1.4911 (lit.[14d] n^{20}_{D} 1.4915), and α-methylstyrene (44%), n^{20}_{D} 1.5382 (lit.[14e] n^{20}_{D} 1.5363), infrared spectra identical with published ones (API No. 295 and 329).[15]

Hydrogenolysis of 1-Phenylcyclohexanol.—A mixture of 4.4 g. (25 mmoles) of 1-phenylcyclohexanol[19] and 100 ml. (100 mmoles) of dichloroaluminum hydride solution was let stand 4 hr. at room temperature; after the usual work-up there was obtained 3.5 g. (87%) of hydrocarbon, b.p. 66–73° (1 mm.). Analysis by v.p.c. on Carbowax 20 M at 185°, with identification of fractions *via* isolation, showed this product to contain 56% of phenylcyclohexane, n^{20}_{D} 1.5256 (lit. n^{20}_{D} 1.5249,[14f] 1.5255[20]),

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(14) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1940: (a) p. 47; (b) p. 188; (c) p. 60; (d) p. 81; (e) p. 192; (f) p. 265; (g) p. 276.

(15) American Petroleum Institute Research Project 44 (spectrum number indicated in text).

(16) J. H. Lamneck, Jr., H. F. Hipsher, and V. O. Fenn, Natl. Advisory Comm. Aeronaut. Tech. Note, **No. 3154**, 9–10 (1954). (Sadtler Standard Spectra, Philadelphia, 1962, no. 8235 and 8237).

(17) K. v. Auwers, *Ann.*, **422**, 178 (1921).

(18) Sample provided by Professor H. C. Brown.

(19) P. Sabatier and A. Mailhe, *Bull. soc. chim. France*, [3] **33**, 74 (1905).

(20) E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1958).

and 44% of 1-phenylcyclohexene, n^{20}_{D} 1.5690 (lit.[14g] n^{20}_{D} 1.5692). The infrared spectra of each compound showed the bands reported by Eliel, McCoy, and Price.[20]

Hydrogenolysis of *t*-Butylphenylcarbinol.—A sample of *t*-butylphenylcarbinol[21] was recrystallized from petroleum ether (b.p. 30–40°) to m.p. 44.5–45.5°; it gave only one peak by v.p.c. A mixture of 4.10 g. (25 mmoles) of carbinol and 100 ml. (100 mmoles) of 1 *N* ethereal dichloroaluminum hydride was prepared at 0°, held at room temperature for 4 hr., and then heated under reflux for 92 hr. The progress of the reaction was followed by v.p.c. analysis of hydrolyzed aliquots on Carbowax 20 M at 175 and 125°; the results of these analyses are presented in Table I. The reaction mixture was hydrolyzed and the ether solution concentrated and distilled to give 3.0 g. (81%) of crude neopentylbenzene, b.p. 57° (7 mm.), and 0.51 g. (11%) of α-chloroneopentylbenzene, b.p. 50° (1 mm.). Samples of the two products were purified by gas chromatography on Carbowax 20 M at 105° to give pure α-chloroneopentylbenzene, n^{20}_{D} 1.5164 (lit.[8] n^{25}_{D} 1.5142), and pure neopentylbenzene, n^{20}_{D} 1.4875 (lit.[22] n^{20}_{D} 1.4885), with infrared spectra identical with those of authentic samples.[23] The hydrocarbon fraction proved to consist of 96% neopentylbenzene with three other components having longer retention times. The slowest moving minor component had the same retention time as authentic 2-methyl-3-phenyl-2-butene.[21] The three minor components, collected together, had an infrared spectrum indicating the presence of a 1,1-disubstituted olefin (bands at 6.03 and 11.18 μ) and other bands suggesting the presence of 2-methyl-3-phenyl-1-butene.

***cis*-α-Methylstilbene.**—Powdered lithium aluminum hydride (4.6 g., 0.12 mole) was added carefully to a solution of 44 g. (0.32 mole) of aluminum chloride in 100 ml. of anhydrous ether, cooled in an ice bath. The solution was stirred for 1 hr. at room temperature and then cooled with an ice bath. *cis*-2,3-Diphenylacrylic acid,[24] m.p. 172–173° (15.6 g., 0.070 mole), was added carefully with ice cooling, over a 20-min. period, and the mixture was kept in the ice bath for an additional half hour. The solution was let stand at room temperature for 1 day and then heated under gentle reflux for 24 hr.

Excess hydride was destroyed by dropwise addition of 4 ml. of water to the cooled, vigorously stirred reaction mixture. The mixture was then poured onto several volumes of shaved ice. The ether layer was separated, and the aqueous layer was extracted twice with 80-ml. portions of ether. The combined ether extract was extracted with saturated sodium chloride solution, dried over sodium sulfate, and finally distilled under vacuum, to give 9.7 g. (71%) of a mixture of olefins, b.p. 108–126° (2 mm.). Analysis by v.p.c. showed the presence of 81% *cis*-α-methylstilbene, 18% α-benzylstyrene, and 1% *trans*-α-methylstilbene. Two recrystallizations from petroleum ether gave 4.2 g. of pure *cis*-α-methylstilbene (as analyzed by v.p.c.), m.p. 47–48.5° (lit.[25] m.p. 48°). An additional 0.94 g. was recovered from filtrates for a total of 5.1 g. (38%). This material was identical in retention time and infrared spectrum with a sample prepared by Dr. J. T. Rudesill using published methods[9] and repurified by v.p.c. after storage.

***threo*-1,2-Diphenyl-1-propanol.**—Diborane, generated externally from 14.8 g. (94 mmoles) of boron trifluoride etherate and 2.7 g. (70 mmoles) of sodium borohydride,[26] was passed at room temperature into a solution of 18.1 g. (94 mmoles) of *cis*-α-methylstilbene in 70 ml. of diglyme. After 2 hr. at room temperature the solution was cooled to 0° and treated dropwise with 5 ml. of water. After 10 ml. of 3 *M* sodium hydroxide had been added, 10 ml. of 30% hydrogen peroxide was added dropwise, the temperature being kept near 0° by ice cooling. The cooling bath was removed 1 hr. after the addition of peroxide was complete; occasional cooling was necessary to keep the temperature from rising above 45° while the reaction proceeded. When the reaction had subsided the mixture was warmed to 60°. The layers were separated and the aqueous layer was extracted twice with ether. The combined organic solution was washed twice with water and thrice with saturated sodium chloride, dried over sodium sulfate, and concentrated, finally, at about 2 mm. The colorless viscous oil was crystallized three times from pentane to give 12.3 g. of *threo*-1,2-diphenyl-1-propanol, m.p. 33.5–35°; an additional 1.6 g., m.p. 33–35°, was obtained from the filtrates to give a total yield of 70%. The acid phthalate had m.p. 127.5–128.5° (lit.[27] m.p. 128–129°).

The alcohol was identical with material obtained *via* reaction of phenylmagnesium bromide with hydratropaldehyde.[9]

***trans*-α-Methylstilbene** was prepared by dehydration of 1,2-diphenyl-2-propanol (from acetophenone and benzylmagnesium chloride)[28] with acetyl chloride and acetic anhydride[29]; it had m.p. 80–80.5° (lit.[29] m.p. 82°).

***erythro*-1,2-Diphenyl-1-propanol.**—Diborane generated as before was passed into a solution of 23.5 g. (121 mmoles) of *trans*-α-methylstilbene in 120 ml. of dry tetrahydrofuran. The boron intermediate was oxidized as before except that the temperature was maintained at 10–15° for 1 hr. and then at room temperature for 1 hr. The product was isolated as before to give 13.0 g. (50%) of *erythro* alcohol, m.p. 50.5–51.5° (lit.[9] m.p. 50–51°), some loss having occurred due to boiling over of the ether solution during concentration. The acid phthalate had m.p. 151–152° (lit.[27] m.p. 151–152°).

Reduction of *threo* and *erythro* Alcohols.—In the following runs, 21.2 mg. (0.1 mmole) of the alcohol to be reduced was added to 0.4 ml. (0.4 mmole) of 1 *N* ethereal dichloroaluminum hydride. The solutions were let stand at room temperature for the specified times, hydrolyzed on ice, and extracted with ether. The dried extracts were analyzed by v.p.c. on Carbowax 20 M at 225° as mixtures of alcohol, 1,2-diphenylpropane, and chloride, the last being estimated by summing the olefin peaks, which were in about the same ratios as observed by v.p.c. of solutions of the chlorides (following).

The *erythro* **alcohol** in 3 hr. gave 11% alcohol, 25% chloride, and 54% 1,2-diphenylpropane; in 24 hr. the analysis showed 4% chloride and 96% 1,2-diphenylpropane. In the latter run 1,2-diphenylpropane was isolated by preparative v.p.c.; n^{22}_{D} 1.5583 (lit.[30] n^{20}_{D} 1.5585).

The *threo* **alcohol** in 13 min. gave 3% alcohol, 31% chloride, 66% 1,2-diphenylpropane; in 3 hr. the analysis showed 28% chloride, 73% 1,2-diphenylpropane; in 24 hr. the yield was 4% chloride, 96% 1,2-diphenylpropane. In the last run 1,2-diphenylpropane was isolated by preparative v.p.c.; n^{22}_{D} 1.5580.

1,2-Diphenylpropane.—To a solution prepared by adding 3.7 g. (28 mmoles) of anhydrous aluminum chloride to 10 ml. (10 mmoles) of 1 *M* ethereal lithium aluminum hydride was added 2.12 g. (10 mmoles) of *threo*-1,2-diphenyl-1-propanol. The mixture was let stand 3 days at room temperature, poured on ice, and worked up in the usual way to give 1.71 g. (87%) of 1,2-diphenylpropane, b.p. 87–88° (1 mm.), n^{21}_{D} 1.5583 (lit.[30] n^{20}_{D} 1.5585). The infrared spectrum was identical with a published one[31]; v.p.c. analysis indicated no other component present.

***erythro*-1,2-Diphenyl-1-chloropropane.**—*erythro*-1,2-Diphenyl-1-propanol (1.06 g., 5 mmoles) was added to 20 ml. (20 mmoles) of ethereal dichloroaluminum hydride, and the reaction mixture was let stand 7 days at 0° and then poured on ice. The product was worked up in the usual way to the point where ether had been removed (under vacuum at room temperature). The crude product was dissolved in 8 ml. of absolute ethanol and the solution was cooled to −4°. The solid which crystallized was washed twice with cold ethanol to give 275 mg. (23%) of impure *erythro*-1,2-diphenyl-1-chloropropane, m.p. 125–132° dec.; this material was recrystallized twice from hexane to give material with m.p. 138–140° (lit.[10] m.p. 139.5–140.5°). A benzene solution, behaved, on v.p.c. analysis on Carbowax 20 M at 215°, as a mixture containing 44% *trans*-α-methylstilbene, 28% *cis*-α-methylstilbene, and 28% α-benzylstyrene, due presumably to cracking in the preheater.

Anal. Calcd. for $C_{15}H_{15}Cl$: C, 78.08; H, 6.55; mol. wt., 231. Found: C, 78.51, 78.53; H, 6.61, 6.44; mol. wt. (Rast), 220.

The previous crude reduction product before crystallization from ethanol gave, on v.p.c. analysis, 72% of 1,2-diphenylpropane and 28% of a mixture of the three olefins in the ratios given previously.

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threo-**1,2-Diphenyl-1-chloropropane** was prepared from the *threo* alcohol by reaction with purified thionyl chloride[32]; m.p. 52–53.5° (lit.[10] m.p. 54–55°). An ether solution of the chloride behaved like a mixture of 53% *trans*-α-methylstilbene, 24% *cis*-α-methylstilbene, and 23% α-benzylstyrene by v.p.c. on Carbowax 20 M at 215°.

Reduction of *erythro*- **and** *threo*-**1,2-Diphenyl-1-chloropropanes.**—The chloride (23 mg., 0.1 mmole) was added to 0.1 ml. of anhydrous ether and 0.3 ml. of 1 *N* ethereal dichloroaluminum hydride to give solutions comparable in substrate and hydride concentration to those used in the reductions of the alcohols (assuming loss of one equivalent of hydride in the initial fast reaction of alcohol with the reagent). In all other respects these runs were carried out in the same way as those in which alcohols were used as substrates.

The *erythro* **chloride** in 3 hr. gave 93% chloride and 7% 1,2-diphenylpropane. The recovered chloride (unrecrystallized) had m.p. 133–136°.

The *threo* **chloride** in 3 hr. gave 82% chloride and 18% 1,2-diphenylpropane. The recovered chloride (unrecrystallized) had m.p. 48–50°.

The *erythro* **chloride** (23 mg., 0.1 mmole) was added to 1.0 ml. (1.0 mmole) of 1 *N* ethereal dichloroaluminum hydride, and the mixture was let stand 36 hr. at room temperature and then worked up and analyzed as before showing 29% chloride and 71% 1,2-diphenylpropane.

Reduction of 1,2-Diphenyl-2-propanol.—In the first of the following runs 270 mg. (1.25 mmoles) of the prior alcohol[28] was added to 5 ml. (5 mmoles) of dichloroaluminum hydride in ether; the other runs were on a four-fifths scale. The mixtures were let stand at room temperature for the specified amount of time, hydrolyzed, worked up, and analyzed by v.p.c. on Carbowax 20 M at 225°.

A reaction time of 3 min. gave 7% alcohol, 93% hydrocarbon (29% *trans*-α-methylstilbene, 57% α-benzylstyrene, 2% *cis*-α-methylstilbene, 13% 1,2-diphenylpropane).

A reaction time of 2 hr. gave 100% hydrocarbon (13% *trans*-α-methylstilbene, 48% α-benzylstyrene, 39% 1,2-diphenylpropane). Essentially identical results were obtained after 4-hr. reaction at room temperature and also after 48-hr. reaction at 0°. In these three cases the crude product was chloride-free, as indicated by a negative Beilstein test.

1,2-Diphenyl-2-chloropropane.—A solution of 5.3 g. (25 mmoles) of 1,2-diphenyl-2-propanol[28] in 50 ml. of distilled methylene chloride was held at 0° while dry hydrogen chloride, generated from ammonium chloride and concentrated sulfuric acid, was passed through for 1 hr. The solution was dried over sodium sulfate and concentrated at the water pump and finally under 1-mm. pressure (1.5 hr.), the materials being kept at ice-bath temperature throughout. The product was clear and colorless and did not crystallize; it was stored at −4° until use. Like the secondary chlorides of this series, this material was cracked to olefins on attempted v.p.c. analysis on Carbowax 20 M at 225°: 60% *trans*-α-methylstilbene, 15% *cis*-α-methylstilbene, and 25% α-benzylstyrene.

Solutions containing 180–250 mg. of the chloride were heated to boiling in a solvent composed of 10 ml. of water and 20 ml. of acetone, cooled, and titrated with standard sodium hydroxide. This analysis showed the formation of 97% of the theoretical amount of hydrogen chloride. V.p.c. analysis of the hydrolysis product showed the presence of 72% 1,2-diphenyl-2-propanol and 28% of an olefin mixture having the composition 53% *trans*-α-methylstilbene, 5% *cis*-α-methylstilbene, and 42% α-benzylstyrene. The chloride reacted at once with silver nitrate in acetone (15 ml.)–water (5 ml.) solution; the reaction product after 1 hr. at room temperature consisted of 79% 1,2-diphenyl-2-propanol and 21% of olefins in essentially the same proportions. Reaction of equimolar amounts of chloride and aluminum chloride in ether at room temperature (3 hr.) gave a hydrocarbon mixture, m.p. 76–80.5°, analyzed by v.p.c. as 94% *trans*-α-methylstilbene, 3.6% *cis*-α-methylstilbene, and 2.4% α-benzylstyrene.

Reductions of 1,2-Diphenyl-2-chloropropane.—In each of the following runs 110 mg. (0.50 mmole) of the chloride was added to the indicated ethereal reducing agent and the mixture let stand at room temperature (*ca.* 25°) for the indicated length of time. The mixtures were worked up in the usual way and analyzed by v.p.c. on Carbowax 20 M at 215°.

A. **Lithium aluminum hydride** (0.52 ml. of 0.96 *M* reagent, 2.0 mequiv. of hydride; 3 hr.) reduction gave 19% *trans*-α-methylstilbene, 19% α-benzylstyrene, and 62% 1,2-diphenylpropane. Essentially identical results were obtained with 12-hr. reaction time. A slow evolution of gas was observed during the reaction.

B. **Aluminum hydride** (0.39 ml. of 0.96 *M* lithium aluminum hydride plus 17 mg. of aluminum chloride in 1 ml. of ether, 1.5 mequiv. of hydride; 12 hr.) reduction gave 11% *trans*-α-methylstilbene, 12% α-benzylstyrene, and 78% 1,2-diphenylpropane. Evolution of gas was observed during the 1st hr. of reaction.

C. **Monochloroaluminum hydride** reagent was prepared by diluting 10.4 ml. of 0.96 *M* lithium aluminum hydride with a solution of 1.33 g. (10 mmoles) of aluminum chloride in 30 ml. of ether. A white precipitate formed and the reagent solution was obtained by decantation. With 1.0 ml. of reagent (1.0 mequiv. of hydride) and 3-hr. reaction time the yield was 11% *trans*-α-methylstilbene, 10% α-benzylstyrene, and 78% 1,2-diphenylpropane. Vigorous gas evolution occurred.

D. **Dichloroaluminum hydride** [0.5 ml. of 1 *N* dichloroaluminum hydride reagent (0.5 mequiv. of hydride); 3 hr.] reduction gave 74%-*trans*-α-methylstilbene, 2% *cis*-α-methylstilbene, and 24% 1,3-diphenylpropane; with 1.0 ml. of 1 *N* reagent (3 hr.) the yield was 32% *trans*-α-methylstilbene, 23% α-benzylstyrene, and 44% 1,2-diphenylpropane; with 1.5 ml. of 1 *N* reagent (3 hr.) the yield was 28% *trans*-α-methylstilbene, 20% α-benzylstyrene, and 52% 1,2-diphenylpropane.

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